



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Toyohisa OYA et al.

Serial No. 09/809,178

Group Art Unit: 1752

Filed: March 16, 2001

Examiner: Thorl Chea

For: PHOTOTHERMOGRAPHIC MATERIAL AND METHOD FOR
FORMING IMAGES

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner of Patents and Trademarks,
Washington, D.C. 20231

Sir:

I, Toyohisa OYA, a Japanese citizen, working at No.210, Nakanuma Minami-ashigara-shi, Kanagawa 250-0123 Japan, hereby declare and state that I received a Master's Degree from Hokkaido University, the department of Science, the course of Chemistry, in March of 1992, and that I was employed by Fuji Photo Film Co., Ltd. in April of 1992 and since that time I have been principally engaged in research and development of photographic materials, particularly synthesis of the photographic materials and use of the materials in photography and other technical fields, at Ashigara Laboratories of the company.

I declare further that I have read all of the documents contained in the file wrapper of the above-entitled application.

I declare further that the test described below was conducted at my

direction and under my supervision and the test results are true and correct to the best of my knowledge.

EXPERIMENT 1: Evaluation of Comparative Photothermographic Materials

Photothermographic materials 121 and 122 were prepared in the same manner as the preparation of Photothermographic materials 101-120 of Example 1 in the present specification except that 157 μ mol of Reducing Compound D-101 and 157 μ mol of Reducing Compound D-119, respectively, were used as the reducing agent in the coating solution for the emulsion layer.

Photothermographic materials 121 and 122 were subjected to light-exposure and heat-development, and then Dmax and fog were evaluated as in Example 1 of the present specification.

Results are shown in the following table.

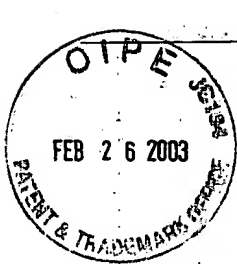


Table 1

Sam ple No.	Reducing agent 1		Reducing agent 2		119°C for 20 seconds (A)			117°C for 20 seconds (B)			115°C for 20 seconds (C)			After storage at 50°C			
	No.	Amount (μ mol)	No.	Amount (μ mol)	Dmax	Fog	Sensit ivity	Dmax	Fog	Sensit ivity	Dmax	Fog	Sensit ivity	Sam ple	Dmax	Fog	Sensit ivity
101	I-1	15.7			1.46	0.12	0.00	0.94	0.11	-0.22	0.41	0.10	-0.49	(A)	1.21	0.12	-0.29
102	II-1	15.7			0.35	0.09	-	-	-	-	-	-	-	-	-	-	-
103	D-101	15.7			-	Strong	-	1.76	0.17	0.45	1.53	0.13	0.31	(C)	1.47	0.13	0.20
104	D-119	15.7			-	Strong	-	1.55	0.13	0.33	1.49	0.11	0.25	(C)	1.45	0.11	0.19
105	D-137	15.7						1.51	0.12	0.26	1.48	0.10	0.17	(C)	1.40	0.10	0.15
106	I-1	15.7	D-101	157	1.59	0.12	0.17	1.53	0.10	0.07	1.48	0.09	0.01	(B)	1.41	0.09	0.02
107	I-1	15.7	D-115	157	1.51	0.12	0.13	1.46	0.10	0.01	1.31	0.09	-0.07	(B)	1.25	0.09	-0.03
108	I-1	15.7	D-119	157	1.50	0.11	0.16	1.49	0.10	0.05	1.33	0.09	-0.02	(B)	1.27	0.09	0.01
109	I-1	15.7	D-137	157	1.47	0.12	0.15	1.43	0.11	0.01	1.39	0.09	-0.12	(B)	1.24	0.09	-0.04
110	I-6	15.7	D-101	157	1.55	0.12	0.15	1.39	0.10	0.04	1.15	0.09	0.00	(B)	1.35	0.09	0.01
111	I-6	15.7	D-115	157	1.47	0.12	0.12	1.35	0.10	-0.02	1.10	0.09	-0.02	(B)	1.31	0.09	-0.03
112	I-6	15.7	D-119	157	1.57	0.12	0.15	1.42	0.10	0.03	1.17	0.09	-0.01	(B)	1.36	0.09	0.00
113	I-6	15.7	D-137	157	1.39	0.12	0.13	1.35	0.10	-0.02	1.07	0.09	-0.13	(B)	1.29	0.09	-0.04
114	I-12	15.7	D-101	157	1.61	0.13	0.18	1.56	0.11	0.10	1.52	0.10	0.05	(B)	1.44	0.10	0.04
115	I-12	15.7	D-115	157	1.53	0.12	0.14	1.48	0.11	0.07	1.40	0.10	0.00	(B)	1.31	0.10	0.03
116	I-12	15.7	D-119	157	1.56	0.12	0.18	1.52	0.11	0.10	1.42	0.10	0.03	(B)	1.35	0.10	0.05
117	I-12	15.7	D-137	157	1.51	0.12	0.17	1.46	0.10	0.05	1.39	0.09	-0.05	(B)	1.29	0.10	0.00
118	I-5	15.7	D-119	157	1.53	0.12	0.14	1.49	0.11	0.08	1.38	0.09	0.01	(B)	1.20	0.10	0.03
119	I-5	15.7	D-137	157	1.47	0.12	0.13	1.42	0.10	0.03	1.30	0.09	-0.07	(B)	1.08	0.09	-0.02
120	II-1	15.7	D-119	157	1.21	0.10	0.05	1.14	0.10	0.00	0.97	0.09	-0.15	(B)	0.88	0.09	-0.06
121			D-101	157	0.05	0.05	-	0.05	0.05	-	0.05	0.04	-	-	-	-	-
122			D-119	157	0.06	0.05	-	0.05	0.05	-	0.05	0.05	-	-	-	-	-

Sample Nos. 101, 102, 121 and 122 are comparative examples.

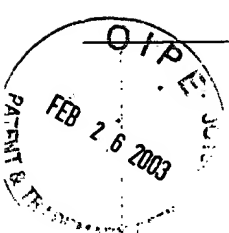
Table 1 shows that particularly preferable results can be obtained by using a reducing compound represented by Formula (1) and a reducing compound represented by Formula (2) or (3) in a photothermographic material.

Sample 101, that only contains 15.7 mmol of Reducing Compound I-1 falling within Formula (2) as a reducing agent, showed poor sensitivity, particularly when it was developed at a lower temperature. Samples 103 and 104, that contain 15.7 mmol of Reducing Compounds D-101 and D-119 falling within Formula (1), respectively, showed a higher sensitivity but serious fog, particularly when they were developed at 119 °C. Samples 121 and 122, wherein the content each of Reducing Compounds D-101 and D-119 was reduced to 157 μ mol that is 1/100 of those in Samples 103 and 104, were not developed actually and showed no sensitivity.

2 Samples 106-109, that contain 15.7 mmol of Reducing Compound I-1 falling within Formula (2) and 157 μ mol of the reducing compounds falling within Formula (1), unexpectedly showed remarkably improved sensitivity, particularly when they were developed at a lower temperature. Such a remarkable improvement in sensitivity can be observed by merely adding a compound represented by Formula (1) in such a small amount that shows no sensitivity in the absence of other reducing compounds, to a photothermographic material containing a reducing compound represented by Formula (2). This is a superadditive improvement.

Similar remarkable improvement can be observed by adding a compound represented by Formula (1) to a photothermographic material containing a reducing compound represented by Formula (3). Please refer to the results of Samples 102, 120 and 122.

I believe that no one skilled in the art could have readily predicted that the combination of the reducing compounds represented by Formula (1) and the reducing compounds Formula (2) or (3) creates such a superadditive improvement when the claimed invention was made.



In order to elucidate the mechanism of the superadditive improvement, I conducted Experiments 2 and 3 described below.

EXPERIMENT 2: Measurement of Oxidation Potential of Reducing Compounds

A polarographic test solution was prepared by dissolving 5×10^{-5} mol of Reducing Compound I-1 in 30 ml of tetrahydrofuran and adding thereto a Britton-Robinson buffer solution in such an amount that gave a total amount of 50 ml. In order that pH of the test solution was adjusted to 6.0 by the addition, pH of the Britton-Robinson buffer solution had been controlled. From the resultant test solution, 15 ml was placed in a cell and Ar gas was introduced for 5 minutes. Then, oxidation potential was measured in the polarographic analyzer P-1100 manufactured by Yanako Analytical Instruments Corp (working electrode: graphite, counter electrode: platinum, reference electrode: saturated calomel electrode, starting potential: -300 mV, scan rate: 20mV/s).

Reducing Compounds I-3, I-4, I-12, D-101, D-115, D-119, D-137 and D-164 were also measured in the same manner.

The results are shown in the following tables.

Table 2

Reducing Compound represented by Formula (1)	Oxidation Potential (V)
D-101	0.42
D-115	0.56
D-119	0.43
D-137	0.47
D-164	0.42

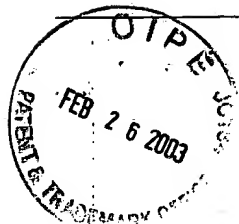


Table 3

Reducing Compound represented by Formula (2)	Oxidation Potential (V)
I-1	0.66
I-3	0.69
I-4	0.60
I-12	0.66

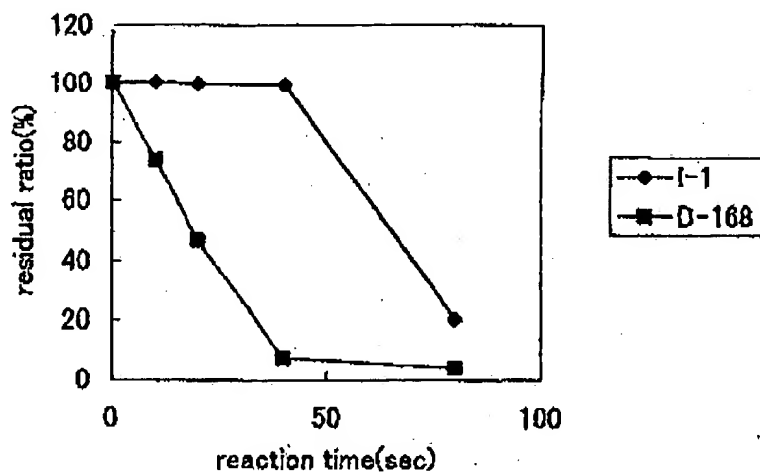
EXPERIMENT 3: Measurement of Consumption Rate of Reducing Compounds

Test sample was prepared in a test tube by mixing 1.2 mmol of silver behenate, 0.043 mmol of silver bromide, 0.43 mmol of Reducing Compound I-1, 0.24 mmol of 6-isopropylphthalazine, 0.083 mmol of 4-methylphthalic acid, 0.043 mmol of Reducing Compound D-168 and 3 ml of dimethyl acetate. The test sample was heated at 120 °C for 80 seconds. A small amount of the test sample was taken out at the predetermined times and analyzed by HPLC to determine residual ratio of Reducing Compound I-1 and Reducing Compound D-168.

The results are shown in the following Figure.

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Fig.1



Tables 2 and 3 show that oxidation potential of the reducing compounds represented by Formula (1) is lower than that of the reducing compounds represented by Formula (2) or (3) and accordingly the reducing compounds represented by Formula (1) have a higher reducing power than the reducing compounds represented by Formula (2) or (3).

Fig.1 shows that Reducing Compound D-168 falling within Formula (1) was rapidly consumed just after beginning of the heating and Reducing Compound I-1 falling within Formula (2) started to be consumed after complete consumption of Reducing Compound D-168.

In order to have the photosensitive silver halide developed, it is thought to be necessary to present four or more Ag(0) atoms in a latent image. Please refer to T. H. James, The theory of the photographic process, 4th edition, chapter 4, pp.111-112.

The reducing compounds represented by Formula (1) have -NHNH- moiety, which is readily adsorbed on silver halide. I understand that the reducing compounds represented by Formula (1) can diffuse in a photothermographic material during a development process to introduce an electron to a photosensitive silver halide whereby, for example, a latent

image only having three or less Ag(0) atoms due to underexposure is changed to a developable latent image and a latent image having four or more Ag(0) atoms is changed to that having more Ag(0) atoms. Silver halide in which a developable latent image is formed remarkably enhances reduction of a silver salt of an organic acid present in the vicinity of the silver halide by the reducing compound represented by Formula (2) or (3). I understand that this is the mechanism of the superadditive sensitization enabled by using the reducing compounds represented by Formula (1) in combination of the reducing compounds represented by Formula (2) or (3). I believe that this is not described or suggested in any documents published before the claimed invention was made.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application of any patent issuing thereon.

Dated this th day of February, 2003.

Toyohisa OYA